Effect of Si and Mn on Microstructure of Biomedical Co-Cr-Mo-C-N Alloys

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学位授与年月日	平成２３年９月１４日
学位授与の根拠法規	学位規則第４条第１項
研究科、専攻の名称	東北大学大学院工学研究科（博士課程） 材料システム工学専攻
学位論文題目	Effect of Si and Mn on Microstructure of Biomedical Co-Cr-Mo-C-N Alloys 生体用 Co-Cr-Mo-C-N 合金の組織に及ぼす Si および Mn 添加の影響
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論文内容要旨

It has been predicted that by the end of 2030, the number of total hip replacements will increase by 174% and total knee arthoplasties will grow by 673% from the present rate. In order to improve the quality of life (QOL) of these patients, further improvements of metallic biomaterial such as Co-Cr-Mo alloys are required in dental and medical technologies with regard to reconstruction of the human body. Cast Co-Cr-Mo-C alloys are widely used in surgical implants owing to their high wear and corrosion resistance, excellent mechanical properties and biocompatibility. Precipitates in the Co-Cr-Mo alloys are known to affect the wear and corrosion-resistant properties of castings as well as the workability of forgings. The control of the type, morphology, size, content and distribution of the precipitates is essential for establishing reasonable production processes of Co-Cr-Mo alloy implants. Heat treatments such as hot-isostatic pressing (HIP) are usually subjected to the cast alloys to improve their properties. Another purpose of the heat treatment is to decrease the precipitate content for improving the workability in following forging or drawing processes. The addition of Si and Mn to the Co-Cr-Mo alloys also affects the precipitate behavior from the view point of its dissolution and formation, as well as carbon and nitrogen. In Co-Cr-Mo alloys, Si and Mn possess the characteristics to stabilize hcp ε-phase and fcc γ-phase, respectively. In this study, the effects of Si and Mn on precipitates in the biomedical Co-Cr-Mo-C-N alloys before and after heat treatment have been investigated.

Experimental Procedures

The chemical composition of the alloys used in this study is listed in Table 1. The alloy is referred to by the name in the left column of Table 1. After the alloys were placed in the sealed SiO_2 ampoule, heat treatments were performed in a horizontal electric resistance tube furnace. The atmosphere inside the ampoule was either high vacuum or argon. The solution-treatment and aging were carried out at temperatures of 1448–1548 K and 873–1473 K, respectively, followed by water quenching. The maximum holding time for the heat treatments was 43.2 ks.

Table 1 Chemical composition of the Co-Cr-Mo alloys used in this study (mass%)

Abbreviation	Cr	Mo	C	N	Si	Mn	P	S	Co
0.5Si0Mn	27.24	5.74	0.22	0.003	0.58	0.02	<0.001	<0.001	Bal.
1Si0Mn	29.17	6.22	0.23	0.005	0.96	0.08	<0.001	<0.001	Bal.
2Si0Mn	28.05	6.01	0.22	0.003	2.60	0.02	<0.001	<0.001	Bal.
0Si1Mn	27.86	6.03	0.25	0.003	0.11	0.97	<0.001	<0.001	Bal.
0Si2Mn	27.07	5.80	0.23	0.003	0.07	1.91	<0.001	<0.001	Bal.
0.5Si0.5Mn	27.46	6.01	0.29	0.003	0.60	0.48	<0.001	<0.001	Bal.
0.75Si0.75Mn	28.26	6.23	0.23	0.003	0.85	0.79	<0.001	<0.001	Bal.
1Si1Mn	27.96	6.09	0.26	0.003	0.98	1.02	<0.001	<0.001	Bal.
0.15C1Si	27.06	5.61	0.13	0.003	1.33	0.02	<0.001	<0.001	Bal.
0.35C1Si	27.68	6.04	0.38	0.003	1.20	0.01	<0.001	<0.001	Bal.
1Si0Mn0.175N	27.9	6.17	0.25	0.15	1.21	0.001	0.002	<0.001	Bal.
0Si1Mn0.175N	27.77	6.09	0.24	0.19	<0.001	1.15	0.002	<0.001	Bal.
1Si1Mn0.175N	27.67	6.01	0.24	0.17	1.19	1.15	0.003	<0.001	Bal.
0Si0Mn0.175N	27.65	6.22	0.25	0.19	<0.001	0.001	<0.001	<0.001	Bal.

The microstructures of the as-cast and heat-treated alloys were observed using an optical microscope and a scanning electron microscope (SEM). A field emission electron-probe micro-analyzer (FE-EPMA) and a transmission electron microscope (TEM) were used for compositional and structural analyses of the precipitates, respectively. The precipitates in the as-cast and heat-treated alloys were electrolytically extracted at room temperature in a 10%H_2SO_4 aqueous solution at 2 V. The phases of the extracted precipitates were identified using X-ray diffraction (XRD) with Cu Kα radiation, and the morphologies of the extracted precipitates were observed using SEM.

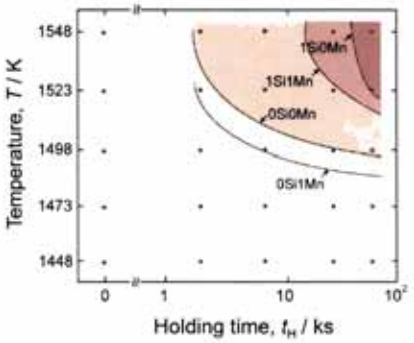

Fig. 1 Heat-treatment conditions for complete precipitate dissolution of precipitates in Co-Cr-Mo-C-Si-Mn alloys.

Microstructure in as-cast and heat-treated Co-Cr-Mo-0.25C-(0-1)Si-(0-1)Mn alloys

In as-cast 1Si0Mn and 1Si1Mn alloys, the precipitates were $M_{23}X_6$-type carbide, η-phase (M_6X-$M_{12}X$-type carbide), and π-phase (M_2T_3X-type carbide with a β-Mn structure), while $M_{23}X_6$-type carbide and η-phase were detected for the as-cast 0Si1Mn alloy. The alloys containing Si required longer heat treatment time for complete precipitate dissolution than 0Si1Mn alloy, as shown in Fig. 1. During the heat treatment, blocky-dense $M_{23}X_6$-type carbide was observed in all the alloys over the temperature range 1448–1498 K. At the heat-treatment temperature of 1523 K, starlike precipitates with stripe patterns—comprising $M_{23}C_6$-type carbide and metallic fcc (face-centered-cubic) γ phase—were detected in 1Si0Mn and 1Si1Mn alloys. A π-phase was observed in the alloys containing Si heat treated at 1523 and 1548 K and in the 0Si1Mn alloy at 1548 K; its morphology was starlike-dense. The addition of Si appeared to promote the formation of the π-phase in Co-28Cr-6Mo-0.25C alloys at 1523 and 1548 K.

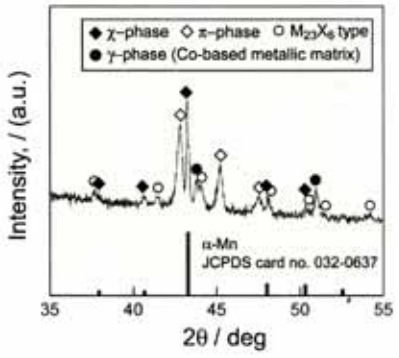

Fig. 2 XRD pattern of the χ-phase precipitate electrolytically extracted from as-cast 0.15C1Si alloy.

Microstructure in as-cast and heat-treated Co-Cr-Mo-(0.15-0.35C)-(0-2)Si-(0-2)Mn alloys

The phase and dissolution of precipitates in the alloys with wider range of Si, Mn and carbon additions, Co-28Cr-6Mo-(0.15–0.35)C-(0–2)Si-(0–2)Mn alloys (mass%), have been investigated. Precipitates detected in the as-cast and heat-treated alloys were $M_{23}X_6$ type, η-phase, π-phase and χ-phase (α-Mn structure). This detection is the first report of χ-phase precipitate in biomedical Co-Cr-Mo alloys. Single η-phase and χ-phase precipitation regions were obtained during the heat treatment of 2Si0Mn and 0.15C1Si alloys, respectively. Si was enriched in the η-phase, χ-phase, and π-phase precipitates and possibly enhanced the formation of these precipitates. Complete precipitate dissolution was observed in all of the alloys except for 0.35C1Si for holding times up to 43.2 ks. Partial melting of the alloys accompanied by π-phase formation delayed the complete precipitate dissolution at high temperatures such as 1548 K, resulting in a C-curved shape of the boundary between the complete and incomplete precipitate dissolution regions in 0Si2Mn, 0.15C1Si, and 2Si0Mn alloys.

Fig. 3 SEM image of the lamellar cellular colony with M_2X type precipitates in 0Si0Mn alloy.

Effect of nitrogen on microstructure in Co-Cr-Mo-0.25C-(0-1)Si-(0-1)Mn alloys

A blocky-dense π-phase precipitate and lamellar cellular colony, which consisted of an M_2X type precipitate and a γ-phase, were mainly detected in the as-cast alloys with and without added Si, respectively. Nitrogen caused the formation of the M_2X type precipitate, but Si appeared to suppress cellular precipitation resulting in the formation of the π-phase precipitate. The microstructure of the lamellar cellular colony in Co-28Cr-6Mo-0.25C-0.175N is shown in Fig. 3. The lamellar cellular colony was suggested to be formed through a discontinuous reaction mechanism, that is, $\gamma_1 \rightarrow \gamma_2 + M_2X$. From the chemical composition analysis, it found that nitrogen was enriched in the M_2X type, η-phase, and π-phase precipitates, but was excluded from the $M_{23}X_6$ type precipitate. Complete precipitate dissolution was observed in all the alloys during heat treatment for up to 43.2 ks. Nitrogen appears to decrease the time required for complete precipitate dissolution at low temperatures. It also delays complete precipitate dissolution at 1548 K due to the enhancement of π-phase formation.

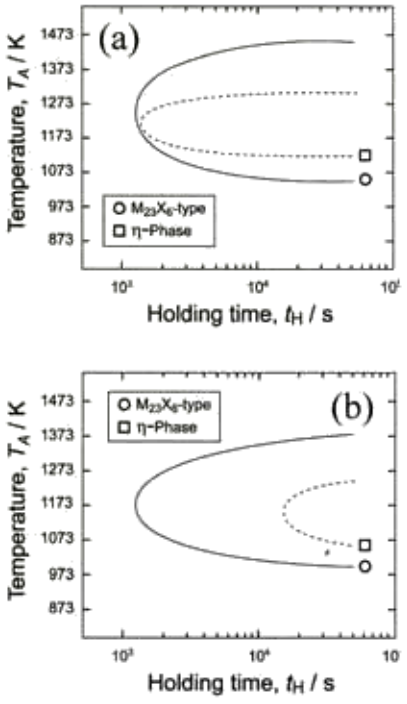

Fig. 4 TTP diagrams of (a) 1Si0Mn and (b) 0Si1Mn alloys during aging.

Aging behavior in Co-Cr-Mo-C-Si-Mn alloys

The effects of the addition of 1mass% Si and 1mass% Mn in Co-28Cr-6Mo-0.25C alloys on aging behavior at 873–1473 K have been investigated. The precipitation area was observed in the aged specimens. The result shows that the precipitation consists of fine

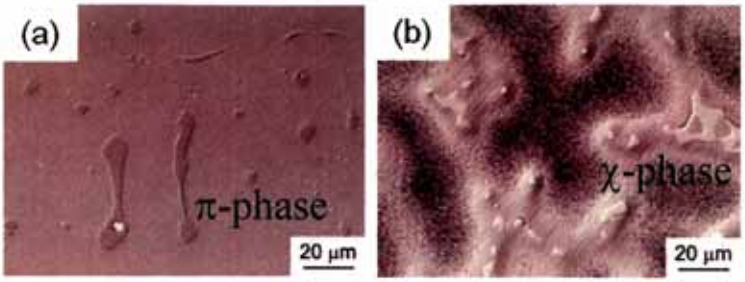

Fig. 5 Surfaces of heat-treated (a) 0.75Si0.75Mn and (b) 0.15C1Si alloys after polarization test in Kokubo solution.

precipitation of $M_{23}X_6$ type and η-phase. Meanwhile, the addition of Mn (Fig. 4(b)) decreased the precipitation area in the Time-Temperature-Precipitation (TTP) diagram as compared to the Si addition (Fig. 4 (a)). The addition of Si increased the precipitation area of η-phase. During aging, precipitate size decreased with decreasing aging temperature. Blocky and rod-like precipitates were observed at higher and lower aging temperatures, respectively. The addition of Si increased the hardness that might be caused by the formation of fine $M_{23}X_6$ type and η-phase precipitates at 1073-1173 K.

Wear and corrosion behavior in Co-Cr-Mo-C-N-Si-Mn alloys

The effect of precipitates on the wear and corrosion properties of Co-Cr-Mo-C-N-Si-Mn alloys was examined. The pin-on-disk type wear test, static immersion, and polarization test were carried out in simulated body fluids of 1mass% lactic acid and Kokubo solutions. The precipitates in the alloys were $M_{23}X_6$ type, η-phase, π-phase, χ-phase, and M_2X type. After wear test, it was found that the ratio of the amount of eluted ions in 1mass% lactic acid solution corresponded to the chemical composition of alloys. The detachment of M_2X type precipitate was observed in as-cast alloy after wear test in 1mass% lactic acid solution. Meanwhile, the amount of elution of metallic ions in 1mass% lactic acid solution during static immersion test was much less than that during wear test. χ-phase drastically decreased the corrosion resistance of the alloy, as shown in Fig. 5. The alloys with χ-phase and $M_{23}X_6$ type precipitates have lower corrosion resistance than those with π-phase and η-phase.

Conclusions

The precipitates observed in as-cast and heat-treated Co-Cr-Mo-C-N alloys with Si and Mn additions were $M_{23}X_6$ type, η-phase (M_6X-$M_{12}X$ type), π-phase (M_2T_3X type with β-Mn structure), χ-phase (intermetallic compound with α-Mn structure), and M_2X type. Si increased the holding time for complete precipitate dissolution during heat treatment. Si was enriched in η-phase, π-phase, and χ-phase precipitates. In contrast, it was excluded from $M_{23}X_6$ type precipitate. Mn decreased the holding time for complete precipitate dissolution at low temperatures during heat treatment. Nitrogen decreased the holding time for complete precipitate dissolution at low temperatures, and enhanced the formation of η-phase and M_2X type precipitates. The M_2X type precipitates detached from metallic matrix during wear test in 1mass% lactic acid solution. The corrosion resistances of alloys with χ-phase and $M_{23}X_6$ type precipitates were inferior to those of π-phase and η-phase in simulated body fluids.

論文審査結果の要旨

Co-Cr 合金は優れた機械的強度に加えて高い耐摩耗性・耐食性を有するため、整形外科、循環器外科、歯科などの分野でインプラント材料として用いられている。特に生体用 Co-Cr-Mo 合金は 1930 年代の開発以来、人工股関節や義歯床に利用されてきたが、近年 Ni フリーCo-Cr 合金として注目されている。Co-Cr-Mo 合金中の析出物は鋳造材および展伸材、いずれにおいてもそれらを利用したデバイス特性や製造プロセスの高度化と関連しており、析出物の相、サイズ、含有量、分布、形状などを厳密に制御する必要がある。本論文は ASTM F75 組成を基本とした生体用 Co-Cr-Mo-C-N 系合金の微細組織、特に析出物の相・形態と熱処理における析出物の形成・溶解挙動、に及ぼす Si および Mn の影響を系統的に調査したもので、全編 7 章よりなる。

第 1 章は序論であり、本論文の背景、関連分野の研究動向および研究目的が記述されている。

第 2 章では、実験に用いる Co-Cr-Mo-C-N-Si-Mn 系合金の組成や合金溶製方法、熱処理条件、組織観察・分析技術、本論文の中核をなす電解抽出を基礎とする析出物分析方法が記述されている。

第 3 章では、Co-Cr-Mo-C-Si-Mn 系合金中の析出物相と熱処理に伴う析出物形成/溶解挙動を解明した。1523 K 以上の熱処理において、$M_{23}X_6$ 型炭化物に加えて starlike 形状を有する π 相（理想組成：M_2T_3X、β-Mn 構造）が形成され、π 相形成は Si 添加により促進されると共に完全析出物溶解を遅延させることを示した。また、従来報告のなかったα-Mn 構造を有する金属間化合物χ相析出物を発見し、その化学組成や形成条件を明らかにした。

第 4 章では、窒素を含有した Co-Cr-Mo-C-N-Si-Mn 系合金中の析出物の挙動を明らかにした。窒素の添加は M_2X 相とη相（$M_{12}X$-M_6X 型）を安定化し、Si 添加は M_2X 形成を抑制することを明らかにした。

第 5 章では、Co-Cr-Mo-C-Si-Mn 系合金の溶体化-時効に伴う硬度上昇の原因が $M_{23}X_6$ 型炭化物およびη相の微細析出にあることを示した。

第 6 章では、Co-Cr-Mo-C-N-Si-Mn 系合金中の M_2X 相およびχ相析出物が耐摩耗性と耐食性を低下させる可能性を示唆した。

第 7 章は総括である。

以上、本論文は生体用 Co-Cr-Mo 合金中の析出物の相構成を Si および Mn 添加の観点から系統的に調査し、新析出相（χ相）を含めた各析出相の安定性に及ぼす元素機能、合金特性に及ぼす析出物相の影響などを明らかにした。これらの成果は医用材料工学の発展に寄与するところが少なくない。

よって、本論文は博士(工学)の学位論文として合格と認める。